Conference Report

Faraday Discussion on the subject of "Nanoalloys": Gold Alloys Prominently Featured

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A Faraday Discussion on the subject of 'Nanoalloys' was held on 3-5 September 2007 in the Chemistry Department, Birmingham University; it was organised by the Royal Society of Chemistry and was attended by some 60 participants, mainly academics from the UK, Europe and the USA. The normal procedure was followed: pre-printed texts were circulated in advance, and authors had only five minutes to present the highlights of their work. There was therefore adequate time for discussion, which was lively and forthright.

The term 'nanoalloy' has been devised to describe very small assemblies of atoms of two or more metallic elements. The term 'cluster' is normally applied to assemblies created in the gas phase, where the number of atoms is typically less than 100, and is countable by mass-spectrometry. It is also used for organometallic compounds stabilised by ligands. The term 'nanoparticle' describes larger assemblies (typically 1-10 nm in size) usually made by chemical routes (e.g. by colloidal methods). Both clusters and nanoparticles can be deposited on supports, where their physical and catalytic properties can be examined. Such assemblies are of considerable current interest, because their properties often differ significantly from those of the corresponding bulk alloys, and homogeneous nanoalloys are sometimes formed from pairs of elements for which the bulk phase diagram shows a large miscibility gap [1].

Of the 25 papers presented, no less than 15 dealt with binary combinations having gold as a member, and of these the palladium-gold pair was the most popular (7 papers). The Discussion was divided into four sections: the first, dealing with Theory and Simulation, can be rapidly dismissed, as most of the work presented seemed to be somewhat remote from the real world. Imaginative structures were devised and their stabilities calculated, irrespective of whether they had been or could be prepared. So, for example, G Barcaro and A Fortunelli (Pisa) used density-functional theory to study the interaction of AgAu clusters with doubly-defective MgO(100), while T Toai, G Rossi and R Fernando (Università di Genova) examined CuAu clusters containing up to 200 atoms; they concluded that gold segregated to the surface, except for N=100, where a near perfect dodecahedron inexplicably showed copper segregation. The formation of bimetallic nanoparticles comprising gold with either nickel, copper, platinum or palladium by collision of clusters of gold and one other kind of cluster was investigated by MM Mariscal and colleagues (Universidad Nacional de Córdoba, Argentina). No paper examined the number of angels that could dance on the tip of a nanoparticle, but such work is probably in progress somewhere.

The second section, on Electronic, Optical and Magnetic Properties, was more practically oriented. Formation of AuAg nanoparticles by low energy cluster-beam deposition onto a transparent support allows measurement of their optical absorption spectra, true alloys showing only a single surface plasmon resonance (E Broyer and colleagues, Université de Lyon I). Laser-vaporisation controlled-deposition has also been used to make AgAu nanoalloys, the wavelength of the single plasman absorption band being a linear function of the gold content (MS El-Shall and associates, Virginia Commonwealth University). Finally in this section, the stability of gas-phase cationic clusters (N<20) containing yttrium, erbium or niobium was investigated using photofragmentation by N Veldeman (KU Leuven).

In the third section, three contributions demonstrated the continuing interest in gold as a catalyst. GJ Hutchings presented the latest results of the Cardiff group on the synthesis of hydrogen peroxide by oxidation of hydrogen using supported PdAu catalysts. In conjunction with work at Lehigh University (Bethlehem, PA) using energy-dispersive X-ray spectroscopy described by CJ Kiely in another paper, it was shown that in PdAu/C catalysts a homogeneous alloy is formed, whereas on TiO_2 and Al_2O_3 the particles have a core-shell structure with palladium in the outer layer. It may migrate there as a result of interaction with oxygen in the air, but it is unclear why this does not happen with carbon as support. Laser vaporisation of bulk alloys of gold with either iron, nickel or titanium provided clusters that could be deposited as Al_2O_3 powder or flat silica, and then examined for selective oxidation of CO in H_2 (PROX reaction). V Caps and colleagues (IRCE, Université de Lyon) showed that the AuTi clusters showed the best activity, and that unsupported AuTi films were also active. These catalysts did not however appear to reach the desired standard of performance [2]. Lastly in the catalysis section PA Sermon and associates (University of Surrey) advocated the use of hydrocarbon conversions (hydrogenolysis and isomerisation) for characterising the surface of PtAu/C catalysts, showing the utility of this conception through the use of *n*-hexane and methylcyclopentane.

The final section was devoted to Structural Studies, and here the popularity of the palladium-gold system was clearly demonstrated, four of the six papers being concerned with it. Highly size-controlled synthesis of nanoparticles of this system was achieved by inert gas condensation on a

sputtering reactor; particles made in this way were homogeneous alloys, with no tendency to core-shell structure (E Pérez-Tijerina and colleagues, Universidad Autónoma de Nuevo Léon, México). Annealing of a TiO_2(110) surface altered the defect density, and variation of the sequential deposition of palladium and gold atoms afforded control over cluster size and distribution (P. Han and DW Goodman, Texas A and M University). CR Henry and colleagues (Campus de Luminy, Marseille) reported that atomic deposition of these elements under UHV onto an Al_2O_3 film produced regular hexagonal arrays of bimetallic particles. Z-Y Li and others (University of Birmingham) showed that AgAu particles made by the inverse micelle method, and having either homogeneous or core-shell structures, could be analysed by scanning transmission electron microscopy in the high-angle annular dark-field imaging mode. Finally O Hampe and colleagues (Institute for Nanotecnology, Karlsruke) formed Au and AgAu cationic clusters (N<20) in the presence of CO, and by using a Fourier-transform ion cyclotron resonance mass-spectrometer were able to see a decrease in CO binding energy with increasing gold cluster size and with increasing silver content.

Three particular impressions were left in the mind after this meeting. (1) The extreme sophistication of the equipment, experimental and theoretical, available and necessary for the observation and study of nanoalloy particles. (2) In contrast to the detailed physical characterisation that these methods allow, the study of catalytic performance is conducted in a desultory and sometimes amateurish fashion, thus limiting the utility of the structural information in accounting for the catalysts. (3) Although, as noted at the outset, many of the systems shown to form homogeneous nanoalloy particles exhibit limited miscibility in the bulk state; an example of this is the platinum-gold pair, the behaviour of which has recently been considered [1], it was disappointing that theoreticians chose not to examine this problem, at least using a molecular orbital approach comprehensible to a chemist. Evidently there is a change in the use to which valence orbitals are put as particle size grows, but the transition from microscopic to macroscopic behaviour was not explored.

The texts of the papers and the discussions will be published later in 2007 by the Royal Society of Chemistry; it should be a fascinating volume.

References

1 GC Bond, Platinum Metals Review, 2007, **51**, 63.

2 GC Bond, C Louis and DT Thompson, Catalysis by Gold, ICP, London, 2006, ch.7.